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(71) Applicant(s)

Peter Gamon Johns

39 Richmond Drive, Watford, Hertfordshire,
WD1 3DQ, United Kingdom

(72) Inventor(s)

Peter Gamon Johns

(74) Agent and/or Address for Service

Forrester Ketley & Co

Forrester House, 52 Bounds Green Road, LONDON,
N11 2EY, United Kingdom

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(56) Documents Cited

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(54) Abstract Title

A silver/copper/germanium alloy composition

(57) A silver/copper/germanium alloy comprising a silver content of at least 50% by weight, a germanium content of between 0.10 and 3% by weight, an elemental boron content of 100ppm or less and an additive content of 2% or less by weight, the remainder principally being copper, the additive content comprising one of, or a combination of, tin, antimony, silicon and indium.

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"A silver/copper/germanium alloy composition"

THE PRESENT INVENTION relates to a silver/copper/germanium alloy composition.

GB 2 255 348 discloses a silver based ternary alloy and more particularly, a silver/copper/germanium alloy having a germanium content of between 0.5 to 3% by weight. Silver/copper/germanium alloys such as those disclosed in GB 2 255 348 provide improved mechanical and fire stain resistant properties over silver/copper alloys without a germanium content. However, these silver/copper/germanium alloys can still be improved upon over the complete range of germanium content.

For example, when such silver/copper/germanium alloys with a high germanium content (1% by weight or greater) are subjected to soldering or annealing operations, at temperatures over 700°C, heat distortion such as sagging can occur. It is thought that the heat distortion is due to an excess of or high concentrations of low melting phases. Another disadvantageous property is that at high soldering temperatures and during annealing when temperatures exceed 700°C, alloys with a low germanium content (1% by weight or less) have a reduced fire stain resistance.

It has also been noted that whilst reduction rates when rolling a cast alloy having a germanium content in the region of 1.5% and a silver content in the region of 80 to 83% are in the region of 90%, the reduction rate drops to in

the region of 40% before edge cracking begins when the germanium content is greater than 1% and the silver content is greater than 90%.

It is an object of the present invention to provide an improved silver/copper/germanium alloy. More particularly, it is an object of the present invention to seek to provide a silver/copper/germanium alloy which does not suffer from one, some or all of the above mentioned disadvantageous properties.

Accordingly, one aspect of the present invention provides a silver/copper/germanium alloy comprising a silver content of at least 50% by weight, a germanium content of between 0.10 and 3% by weight, an elemental boron content of 100ppm or less and an additive content of 2% or less by weight, the remainder principally being copper, the additive content comprising one of, or a combination of, tin, antimony, silicon and indium.

Advantageously, the additive content is between 0.01 and 1%.

Preferably, the additive content is in the region of 0.2%.

Advantageously, the boron content is 20ppm or less.

In order that the present invention may be more readily understood, it will now be described, by way of examples.

As previously mentioned, silver/copper/germanium alloys can suffer from a number of disadvantageous properties such as: sagging during soldering or annealing, a reduction in fire stain resistance at high temperatures (e.g. during annealing) and reduced reduction rates when rolling cast alloys.

The addition of a minor amount of tin, antimony, silicon or indium to a silver/copper/germanium alloy having an elemental boron content has been found to ameliorate one, some or all of these problems.

Over the germanium content range of 0.1% to 3%, it has been found that the addition of tin, antimony, silicon or indium in small quantities, less than 2% by weight, brings advantages in that the mechanical properties of the resultant silver/copper/germanium alloy are improved. For example, heat distortion such as sagging of the silver/copper/germanium alloy at high solder temperatures is reduced, the alloy can be more readily rolled further from the as cast state and the alloy does not work harden so quickly during other cold work processes.

In one example, a silver/copper/germanium alloy having a germanium content of 1% includes a tin content of between 0.01 and 1%. The silver/copper/germanium alloy also has an elemental boron content of 100ppm or less. The addition of the tin positively influences the distribution of the low melting point eutectics. The low tin content causes a reduction in coarse dendritic formations and secondary dendritic arms. Thus, excessively high concentrations of low melting point phases which predispose the alloy to heat distortion are avoided and the resultant alloy is therefore less susceptible to heat distortion at high soldering temperatures (typically $>700^{\circ}\text{C}$) than the same silver/copper/germanium alloy would be without the tin content. The effects of using antimony, silicon or indium in place of tin as an additive are comparable. Additionally, beneficial effects are achievable with an additive comprising a combination of any or all of tin, antimony, silicon or indium.

Another example provides a cast silver/copper/germanium alloy having a germanium content of 1%, a tin content of 0.2% and an elemental boron

content. Boron is present in the alloy at less than 100ppm. The resultant cast silver/copper/germanium alloy is suitable for rolling and will reduce by 90% before edge cracking occurs. This is at least twice that of the comparable silver/copper/germanium alloy with a germanium content of 1% or greater and without a tin, antimony, silicon or indium content which would have a maximum reduction of between 40 to 50%.

A further example provides a silver/copper/germanium alloy having a germanium content of between 0.3 and 1.1%, a tin content of 0.2% and an elemental boron content. Boron is present in the alloy at less than 100ppm. The resultant silver/copper/germanium alloy is fire stain resistant even at high soldering and annealing temperatures ($>700^{\circ}\text{C}$) at which comparable silver/copper/germanium alloys without a tin, antimony or indium content would exhibit reduced fire stain resistance.

In the above mentioned examples, the silver content can be as low as 50% by weight with the remainder content principally being copper. Preferably, the silver content is as low as 50% by weight with the remainder content being copper apart from any impurities. Elemental boron is required to be present in accordance with the present invention. A boron content of 20ppm is preferred but the boron content should be constrained at 100ppm or less.

For cast silver/copper/germanium alloys with germanium contents of 1.5% to 3%, it is preferable that the silver content is greater than 90% and most preferably, greater than 92.5%, which ranges have been found to be particularly advantageous for good reduction rates when rolling the cast alloy.

For silver/copper/germanium alloys with germanium contents of 1.1% or less, it has been found that the addition of a tin, antimony or indium content of

2% or less preserves the fire stain resistance of the resultant silver/copper/germanium alloy. As such the germanium content can be reduced to between 0.3 to 1%.

The addition of tin, antimony, silicon or indium further improves (most notably with the antimony and silicon additives) the tarnish resistance of silver/copper/germanium alloys. The addition appears to be protecting the copper in the alloy. Earlier tarnishing tests on binary silver/germanium alloys showed that the silver in binary silver/germanium alloys was protected almost completely from tarnishing by the germanium. However, ternary alloys with copper such as those proposed by the present invention (but without a tin, antimony, silicon or indium addition) showed a discolouring of the alloy from copper oxide and sulphide even though no silver sulphide was formed.

Due to a reduction in the amount of copper present in the alloys embodying the present invention (as a result of the presence of the additive content), it is desirable to improve the hardness of the silver/copper/germanium alloys embodying the present invention. This can be achieved by adding a small amount of nickel to the alloy, preferably from 0.01 to 2% by weight.

For the sake of clarity, it should be noted that where the present specification refers to a boron content of less than 100ppm or an additive content of 2% or less, it is always essential that, in the silver/copper/germanium alloy according to the present invention, there is both a boron content and an additive content of greater than zero. The boron is elemental boron.

A master alloy comprising copper, germanium, boron and the additive content of tin, antimony, silicon or indium is a convenient means of delivering the constituent parts of the alloy embodying the present invention in a form

which can simply be combined with silver to produce the resultant silver/copper/germanium alloy. If the resultant alloy also requires a nickel content, then the nickel content would be one of the constituents of the master alloy.

The benefits achieved by the present invention can be attributed to the addition of tin, antimony, silicon or indium contents to the silver/copper/germanium alloy. As well as achieving these benefits by adding tin, antimony, silicon or indium individually, the benefits can also be achieved by adding tin, antimony, silicon or indium contents in any combination with one another, the total additive content not exceeding 2% by weight.

The additive content of tin, antimony, silicon or indium is 2% by weight or less of the resultant silver/copper/germanium alloy. Conveniently, the additive content should be between 0.01 and 1% by weight. Preferably, the additive content is in the region of 0.2% by weight.

CLAIMS:

1. A silver/copper/germanium alloy comprising a silver content of at least 50% by weight, a germanium content of between 0.10 and 3% by weight, an elemental boron content of 100ppm or less and an additive content of 2% or less by weight, the remainder principally being copper, the additive content comprising one of, or a combination of, tin, antimony, silicon and indium.
2. An alloy according to Claim 1, wherein the additive content is between 0.01 and 1% by weight.
3. An alloy according to Claim 2, wherein the additive content is in the region of 0.2% by weight.
4. An alloy according to any preceding claim, wherein the silver content is 80% or greater.
5. An alloy according to any preceding claim, wherein the silver content is 83% or greater.
6. An alloy according to any preceding claim, wherein the silver content is 92.5% or greater.
7. An alloy according to any preceding claim, wherein the germanium content is 1.1% or less.
8. An alloy according to any preceding claim, wherein the germanium content is between 0.3 and 1.1%.

9. An alloy according to any preceding claim, wherein the germanium content is between 0.9 and 1%.
10. An alloy according to any one of Claims 1 to 6, wherein the germanium content is between 1.5% and 3%.
11. An alloy according to any preceding claim, wherein the boron content is 20ppm or less.
12. An alloy according to any preceding claim, wherein the boron content is 20ppm.
13. An alloy according to any preceding claim, including a nickel content of from 0.01 to 2% by weight.
14. An alloy according to any preceding claim, wherein the remainder is copper apart from any impurities.
15. A copper/germanium master alloy having a copper, germanium, boron and additive content for the production of a silver/copper/germanium alloy according to any preceding claim, the additive content comprising one or a combination of tin, antimony, silicon and indium.
16. A copper/germanium master alloy according to Claim 15, wherein the master alloy also includes a nickel content.
17. An silver/copper/germanium alloy substantially as hereinbefore described.

18. Any novel feature or combination of features disclosed herein.



Application No: GB 9926313.9
Claims searched:

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Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C7A

Int Cl (Ed.7): C22C 5/00

Other: On line databases WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	WO 95/14112 A Apecs see example 2	Claim 1 at least
X,Y	WO 96/22400 A Apecs see table 1	.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.